Simulation and Theory of Supercooled Liquids and Glasses

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Supercooled liquids are common in nature, such as low-temperature biological systems and clouds. Glasses, typically formed by rapid supercooling of the liquid melt, are essential in many industrial applications, for example in polymers, pharmaceutical preservation, and corrosion-resistant alloys. Despite their prominence, our theoretical understanding of these substances is rather incomplete and many questions remain concerning their thermodynamic treatment, the relationship between their kinetics and thermodynamics, and the connection between molecular architecture and macroscopic behavior. We present our recent work, which aims to clarify some of these questions. In one case, we focus on the possible basis for and detection of a low-temperature, metastable liquid-liquid coexistence in simulated water and silica [see, for example, Mishima and Stanley, Nature 396, 329 (1998)]. Despite several encouraging low-temperature simulation studies, there are still no results that unambiguously identify the existence of (or lack thereof) a first-order liquid-liquid transition in these systems. We use robust and relatively new simulation algorithms based on the Wang-Landau protocol [PRL 86, 2050 (2001)] to determine, without using an explicit temperature, the thermodynamics of supercooled water and silica. In doing so, we clarify the nature of the low-temperature transition and its relationship to details of the intermolecular potential. We also present a theoretical framework for liquids, based on the energy landscape ideas of Stillinger and Weber [PRA 25, 978 (1982)], which has important implications for glasses. This theory clarifies and shows important distinctions among several glassy phenomena, including the so-called Sastry density, Kauzmann transition, and "ideal" glass transition. As a part of this work, we also develop a landscape-based minimum model for simple liquids at low temperatures whose equation of state shows reasonably good agreement with simulation results.